Enhanced piezoelectric effect at the edges of stepped molybdenum disulfide nanosheets

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Abstract

The development of piezoelectric layered materials may be one of the key elements enabling expansion of nanotechnology, as they represent a realistic solution for the construction of efficient transducers for a wide range of applications, including self-powered devices. Here, we investigate the piezoelectric effect in multilayer stepped MoS_2 flakes

obtained by liquid-phase exfoliation, which is especially interesting because it may allow the fabrication of scalable electronic devices using large area deposition techniques (e.g. solution casting, spray coating, inkjet printing). By using a conductive atomic force microscope we map the piezoelectricity of the MoS_2 flakes at the nanoscale. Our experiments demonstrate the presence of electrical current densities above 100 A/cm^2 when the flakes are strained in the absence of bias, and the current increases proportional to the bias. Simultaneously collected topographic and current maps demonstrate that the edges of stepped multilayer MoS_2 flakes promote the piezoelectric effect, as the largest currents are seen there. Density functional theory calculations are consistent with the ring-like piezoelectric potential generated when the flakes are strained, as well as the enhanced piezoelectric effect at edges. Our results pave the way to the design of piezoelectric devices using layered materials.

Keywords: Piezoelectricity; MoS_2; liquid-phase exfoliation; CAFM; DFT;

Main text

Piezoelectricity is the property of a material to convert mechanical energy into electrical energy and *vice versa*.[1] The piezoelectric effect appears when the atomic symmetry of a material is broken due to an external mechanical stress,[2] causing the accumulation of electric charges.[2] If a load resistor is connected, the device can produce a net current.[3] This effect has been used in a wide range of applications, including sensors,[4] detectors,[5] transducers[6] and energy harvesters.[7] With the rise of low dimensional materials, the interest in piezoelectric devices has increased considerably, as it is expected to be enhanced with reduced dimensionality.[8] During the last decade, zinc oxide (ZnO) nanowires have been by far the most studied piezoelectric nanomaterials,[9-11] and it has been reported that they are able to generate large current densities (J) above 1 A/cm^2, [12] which is significantly larger than those thus far observed in other clean energy technologies, such as solar cells (~30 mA/cm^2).[13] The presence of piezoelectricity in other low dimensional materials, like layered materials (LMs),

such as hexagonal boron nitride (*h*-BN),[14] doped graphene (with Li, K, H or F),[15-16] or transition metal dichalcogenides (TMDs)[17-20] is even more desirable, since they can provide additional properties, such as large mechanical strength, transparency and high chemical stability.[21-22]

The existence of piezoelectricity in LMs was theoretically suggested in Ref.[14], who calculated that multilayer *h*-BN with an odd number of layers (*n*) shows piezoelectric effect, with intensity inversely proportional to *n*. Ref.[15], based on density functional theory (DFT) calculations, suggested that graphene (which is not inherently piezoelectric[23]) may show small (e_{11} = 0.5 × 10^{-10} C·m^{-1}) out-of-plane piezoelectric response by placing impurities (such as K, H, F and/or Li) on one face. Also using computational methods, Ref.[16] reported that graphene may show even larger (e_{11} = 4.5 × 10^{-10} C·m^{-1}) piezoelectric effect in-plane if its point group symmetry is altered with B or N dopants. Piezoelectricity was also theoretically predicted in TMDs, including MoS_2, $MoSe_2$, $MoTe_2$, WS_2, WSe_2, and WTe_2,[17] with MoS_2 having the largest piezoelectric coefficient (e_{11}= 2.9 × 10^{-10} C·m^{-1}).[18] MoS_2 is also the only TMD in which piezoelectricity has been experimentally verified. Ref.[19] used a programmable electrometer to monitor the voltages generated by mechanically exfoliated MoS_2 flakes (with thicknesses between 1 and 6 layers) when exposed to in-plane mechanical strains. Ref.[20] used an atomic force microscope (AFM) to detect the deflection of suspended 1 to 3 layers thick MoS_2 flakes (obtained by mechanical exfoliation) when subjected to different bias conditions. Refs.[3, 20] further corroborated these observations, identifying MoS_2 as the most promising piezoelectric LM. However, mechanically exfoliated MoS_2[18-19] is not suited to large scale device fabrication,[24] as the size of the flakes used thus far is too small (just hundreds of nanometers, while wafer scale sizes are preferred), plus they often show thickness fluctuations. Chemical vapor deposition (CVD) has been used to grow triangular monolayer MoS_2 flakes with sizes of ~ 6 μm,[3] but the electrodes must be in-situ patterned at specific locations (at the edges of the MoS_2 flakes) by electron beam lithography, which is not easily scalable. To the best of our knowledge, the presence of piezoelectricity in MoS_2 flakes obtained using liquid-phase exfoliation (LPE),[25-27] has never been reported. Moreover, while

refs.[3, 18, 20] investigated the presence of piezoelectricity in MoS_2 at the nanoscale using an AFM, we are not aware of any work reporting nanoscale mapping of the piezoelectric effect.

Here we map piezoelectricity in MoS_2 flakes at the nanoscale using a conductive atomic force microscope (CAFM). Stepped (pyramidal) multilayer MoS_2 flakes produced by LPE[25-27] are deposited on a silicon substrate with holes, and the suspended membranes are scanned with the tip of a CAFM using different contact forces. In the absence of bias, electrical currents up to ~100 pA appear (J = 100 A/cm^2), and they increase with the contact force. Current maps with sizes down to 250 nm × 250 nm reveal that the MoS_2 edges generate piezoelectric currents much larger than any other feature in the sample. The scalability of LPE is an important step towards the use of this material in large area printed electronics,[28] for applications such as self-powered devices,[28] piezoelectric transformers,[29] and antennas.[30]

The MoS_2 ink is prepared by dispersing 4 mg of MoS_2 powder (purchased from Alfa Aesar) in 10 mL isopropyl alcohol (IPA) using an ultrasonic bath (KQ-100KDB High Power NC, Kunshan Ultrasonic Instruments) at a power of 90 W for 26 hours. The thin flakes and the larger particles are separated using a H1650-W centrifuge (from Cence Instrument) working at 4000 rpm (2500g) for 15 minutes, which forms a supernatant rich on thin MoS_2 flakes (Figure 1a). For characterization and device fabrication, only the supernatant is utilized.

The MoS_2 ink (Figure 1a) is drop-cast onto an n^{++}-Si wafer substrate and allowed to dry naturally for 5 hours. Scanning electron microscopy (SEM) shows that the substrate is almost completely covered with MoS_2 flakes (Figure 1b). The flakes exhibit squared/rhomboid shapes with an average lateral size of 6.67 μm ± 2.38 μm, as corroborated by statistically analyzing more than 1000 flakes (see Figure S1 in Supporting Information, SI). This large size (compared to other works[25] and commercially available products[31]) may be related to the low power used during the ultrasonication step, which is able to overcome the inter-layer Van der Waals forces but not sufficient to significantly disrupt the in-plane covalent framework.[32] High resolution SEM images reveal the stepped nature of the multilayer MoS_2 flakes (Fig.1c). The morphology of the flakes is further characterized by means of topographic AFM maps in

tapping mode (Figure 1d). The stepped nature of the flakes can be seen in the cross section (see Figure 1e). The typical thickness of the flakes is between 5 and 15 nm, and the height of the steps measured in Figure 1e is ~ 0.75 nm. While the ideal thickness of a MoS_2 layer is 0.65 nm,[33] it has been reported that AFM measurements show wider distributions in heights (between 0.6 and 0.9 nm)[34] due to the presence of adsorbates or other interactions between the film and oxide substrate surface.[35] Hence, we assume each step in Figure 1e to corresponds to a MoS_2 monolayer. Thus, our typical MoS_2 flake have *n* between 7 and 20. The Raman spectrum in Figure S2 shows the two fingerprints of (2H) MoS_2 at 383 cm^{-1} and at 409 cm^{-1} corresponding to the E^1_{2g} and A_{1g} modes respectively.[36] Considering the spectral distance between the E^1_{2g} and A_{1g} peaks we conclude that the MoS_2 dispersion predominantly consists of flakes with $n > 6$.

The flakes are also deposited on an n^{++}-Si substrate with holes (see Figure S3 in SI) following the same procedure. Figure 2a shows the SEM image of one such hole before depositing the MoS_2 flakes. Figure 2b shows holes partially and fully covered with flakes. Figures 2d and 2e plot the topographic AFM maps collected on uncovered and covered holes. The presence of a MoS_2 flake blocks the penetration of the tip into the 2.2 μm deep hole, as depicted by the cross sections in Figure 2f. Another factor that corroborates the presence of MoS_2 on the hole is the shape of force-distance (F-d) curves. Figure 2c shows the typical F-d curves collected on both the suspended MoS_2 membrane and on Si (red and blue spots in Figure 2b, respectively). The F-d curve on Si shows the adhesion peak typically observed on rigid materials,[37] manifested as a large negative peak in the retrace curve. On the contrary, the shape of the F-d curve on the MoS_2 flakes shows progressive attachment and detachment, a behavior characteristic of suspended membranes.[20] These results confirm that the MoS_2 flakes successfully cover the holes.

The suspended MoS_2 flakes can be strained by increasing the contact force during the topographic AFM scan. In order to better understand the relation between force and flake deformation, we measure sequences of topographic maps in contact mode by applying different vertical forces with the AFM tip (from 0 to 45 nN). The AFM maps and their cross

sections (Figure 3) reveal a progressive increase of the depth with the applied contact force. The asymmetric shape of the cross-sections at low contact forces is related to the direction of the scan, as indicated in Figure S4 in SI. From Figure 3, some interesting conclusions can be extracted: *i)* in all cases the depths are much smaller than the depth of the hole (see Figure 2f for comparison) corroborating that the shapes observed are related to the morphology of the suspended flakes, not to the shape of the hole; *ii)* the experiment is repeated using different contact force sequences, i.e. varying the contact force from low-to-high values (0 to 45 nN), from high-to-low values (45 to 0 nN), and using randomly selected alternate forces. In all cases, the depth values are repeatable, indicating the reliability and reproducibility of the data in Figure 3; and *iii)* the observation of low depths using low contact forces (~250 nm at 4.5 nN) after high depths using high contact forces (~ 950 nm at 45 nN) confirms the relaxation of the strain in the flakes, and eliminates the possibility of sliding inside the hole. Similar experiments were previously reported for MoS_2[38] and other LMs,[39] with equivalent results. Therefore, Figure 3 corroborates that the flakes are strained for contact forces ranging between 0 and 45 nN.

As multilayer MoS_2 flakes have shown to be piezoelectric,[19] the strained flakes in Figure 3 should generate a potential between different points. We note that different orientations of mechanical strain may generate currents in different directions. Ref.[19] observed that mechanical strains applied in the 'armchair' and 'zig-zag' directions generate currents of opposite polarities. Ref.[3] reported that a vertical force applied with an AFM tip at the center of a MoS_2 flakes generates a net ring-like field in the tip/MoS_2 system, with the positive potential at the tip and the negative at the surroundings. To confirm these results, the experiments in Figure 3 are then repeated using conductive AFM tips, and the current is monitored with varying the contact force (22 – 247 nN). Figure 4a shows that, in the absence of bias, large (~150 pA) currents can be measured on the strained MoS_2 membrane suspended on the hole (indicated with a dotted circle), and no current is generally observed on the bare $n^{++}Si$ (out of the hole). The propagation of the current outside the hole at high contact forces indicates that the MoS_2 flakes may have been folded at that position, a behavior already

known when scanning a LM surface with an AFM tip.[33, 40] In any case, the observation of currents above 150 pA without bias only at the strained areas corroborates the presence of piezoelectric effects, as it was similarly observed in both LMs[19] and nanowires[12]. Ref.[41] reported that a pressure induced semiconductor-to-metal transition can be expected in MoS_2 flakes, with an induced structural phase transfer from the original $2H_c$ to $2H_a$-MoS_2. Ref.[41] identified three characteristic regions under different contact forces: *i)* below 10 GPa, MoS_2 behaves as semiconducting; *ii)* between 10 and 19 GPa, an intermediate state is reached; *iii)* and above 19 GPa, the material behaves as a metal. In our experiments the contact force applied with the tip of the CAFM is limited by the length of the cantilever and the deflection setpoint used, and the maximum we applied is 247 nN (see Figure 4a). As in CAFM experiments the tip/sample contact area is typically 100 nm^2, that gives a pressure of 2.47 GPa, which ensures that we are working within the region of semiconducting character.[41] Therefore, we do not consider the larger currents observed here as a consequence of phase transition or band structure modification in MoS_2. Furthermore, although a strain gradient is induced with the CAFM tip, the observation of current cannot be attributed to the flexoelectric effect, which is negligible in MoS_2 fakes.[42] The total area and volume of the currents generated have been quantified using the WSxM software of the AFM, [43] and a relation to the contact force can be observed in Figure 5, further supporting the link between mechanical strain and current. Note that, in CAFM experiments, an increase of contact force (F_c) usually produces an increase of the tip/sample contact area (A_c),[44] which may increase the currents registered, as $I = J \cdot A_c$ (where I is the total current measured by the CAFM and J is the current density). Nevertheless, this effect cannot explain the observations of current generation in Figures 4 and 5, as they are obtained without bias, and would imply J~0. In other words, the tip/sample contact area effect can explain small current increases (few picoamperes in the presence of bias), but not the large (~150 pA) currents generated in the absence of bias. The currents in Figure 4 are reproducible using both contact mode CAFM and Peak Force TUNA[45], which measures the current in dynamic tapping mode, discarding the effect of parasitic static currents.

The current maps reveal that the areas of the MoS_2 flakes that show large currents follow a correlation to the topographic profile, as displayed in Figures 4b and 4c. On the areas with flat morphology the density of current spots is smaller, while regions full of steps are more active. This behavior can be further analyzed via small area (250 nm × 250 nm) scans. Figure 6a shows the deflection error map collected at a stepped location of the sample. This image is especially interesting because it displays the presence of steps in the MoS_2 better than the topographic map. Figure 6b shows the simultaneously collected current map in the absence of bias. The images reveal a good correlation (see also Figure S5 in SI), indicating that the steps in the multilayer flakes are genuine features promoting the generation of current. The superior piezoelectric effect at the edges could be related to an increased asymmetry due to the exposed S atoms at the edges, as well as the increased density of electrons, which enhances charge transport.[46,47] This is consistent with the observation that taller steps show larger currents (as seen in Figures 6a and 6b), because they should contain larger amount of vacancies, which favor asymmetries in the film and the generation of piezoelectricity. It is worth noting that the areas in Figure 6b that show no current (*i.e.* small steps and plateaus) may be in fact driving currents below the resolution of the CAFM (this setup can only detect currents above 1 A/cm^2). In the case of the plateaus, currents are less likely to be generated due to non-optimal crystal orientation with respect to the tip.[19] Figure 6c superimposes topographic and current cross-section, with a clear step/current correlation. Other special properties related to the exposed atoms at the edges of MoS_2 sheets were previously reported. Ref.[48] theoretically predicted that the edges of MoS_2 may promote the disassociation of water by covalent bonding of oxygen and hydrogen at its zigzag and armchair edges. These hypotheses were experimentally demonstrated in Ref.[46], where the electrocatalytic hydrogen evolution reaction was observed at the edges of monolayer MoS_2 flakes.

The absence of current observed with the CAFM at the flat areas of the MoS_2 nanoseets (at the plateaus, out of the edge region, see Figs. 6b and 6c) is not in conflict with the previous demonstrations of piezoelectricity at MoS_2 sheets with an uneven number layers.[18-19] The reason is that the minimum current density that a standard CAFM can map is ~ 1 A/cm^2

(1 pA flowing through an area of ~ 100 nm^2). Therefore, the currents densities generated at the plateaus (if any) are below 1 A/cm^2, while the edges in the MoS_2 generate current densities above that value, both at regions with an even and uneven amount of layers. In fact, in our experiments it is complex to assess the thickness of the MoS_2 sheet at each location, but we clearly observe that the piezocurrents are generated at all the edges (no spatial alternation is observed, see Figs. 6b and 6c).

In order to get further insights, we perform density functional theory (DFT) calculations. Two structures are considered, *(1)* a single monolayer of MoS_2 deformed with a circular indent (see Figure 7a) to simulate the physical case depicted in Figure 2e, and *(2)* a stepped MoS_2 trilayer (see Figures 7c and 7d) to mimic the experimentally observed steps in Figures 4 and 6. As it is not feasible to perform DFT calculations on the micrometer scale of the experiments, we model similar systems with smaller dimensions (as commonly done in DFT studies).[49] Because DFT calculations scale as N^3, if the size of the system is doubled (number of atoms) the calculation takes 8 times as long. In this work, we presented the largest calculation possible within the framework of DFT. To go to larger systems one would need to sacrifice the accuracy of the calculations (tight-binding or a classical model). More specifically, for structure (*1*) we construct a 4.4 nm × 3.8 nm MoS_2 sheet. To mimic the deformation due to the CAFM tip, we displace the central atoms of the MoS_2 sheet along the vertical axis (see Figure 7a). This deformed circular pattern in the center of the MoS_2 monolayer has a diameter of ~ 2.8 nm. The ratio between diameter and vertical deformation (D/L) is consistent with the experiments. The atoms outside the circular region, which represent the portion of MoS_2 supported by the substrate, are initially given positions corresponding to an unstrained monolayer. Periodic boundary conditions are employed in all directions and periodically replicated MoS_2 layers are separated by 2 nm in the vertical direction, sufficient to eliminate any interaction between neighboring sheets.

Holding the positions of the Mo atoms fixed in this deformed shape, all coordinates of the S atoms are allowed to relax to the lowest energy configuration under the deformation constraint. We then obtain the Löwdin charges[50-51] (the projections of the electron density onto

orthonormalized atomic orbitals) on each atomic site. The partial Löwdin charges are used in Figure 7b to plot the response of the electric charge of a single layer of MoS_2 to the deformation induced by the AFM tip when pushing on the center of the suspended region. No charge separation occurs in the unperturbed flat region, as expected (gray color). Within the depressed region, a net negative charge accumulates around the rim of the circular depression and at the center of the indentation (red colors), while a compensating net positive charge appears in a ring pattern between the rim and the center (blue). A three-fold symmetry is evident in the charge distribution, following the symmetry of the crystal lattice. This result agrees with the direction of the electrical field reported by Qi *et al.*[3], and further supports the generation of a ring-like electric field in the tip/MoS_2 system. These calculations used an energy convergence threshold of 10^{-7} eV. The total energy of pseudopotential based calculations does not have a physical meaning. However, since we have used Projector Augmented Wave (PAW) datasets we can obtain a PAW reconstructed all-electron total energy for the relaxed system, which was approximately -15828800 eV for the 360 atom supercell.

Turning to structure (*2*), we find that the enhanced piezoelectric effect at the step edges is also predicted by DFT. Figure 7d shows a tri-layer MoS_2 sheet formed into a step structure with the steps terminated in the 'zig-zag' pattern. This model also employs periodic boundary conditions in each direction. The ground-state electronic charge density is obtained for two cases: *i)* the structure relaxed to the experimental lattice parameters, and *ii)* the structure relaxed after the lattice parameter is stretched by 2% along the step direction. The isosurfaces in Figure 7d show the change in charge density due to this stretching. Excess electron charge density accumulates along the top of the highest step and the top of the edges of the middle step (silver lobes) while electron density is lost from the underside of these steps (brown lobes). There is little electron density difference at the surface of the bottom sheet. These results are consistent with the observation of increased scanning tunneling microscopy current at the step edges of the stretched sheets[52].

In summary, the piezoelectric properties of liquid-phase exfoliated MoS_2 have been mapped with nanoscale precision. Our experiments demonstrate the generation of abundant

currents without bias application when the MoS_2 flakes are strained. Further, the current increases with the applied force. The lateral resolution of this technique allowed mapping the features that promote piezoelectricity. We found that the edges in the multilayer MoS_2 membranes show the largest currents, up to 148 pA (J = 148 A/cm^2). These results can have important implications in the field of printable electronics, with applications including self-powered devices, sensors, transformers and antennas.

Methods

Piezoelectric effect characterization

In order to characterize the properties of the MoS_2 flakes at the nanoscale, we fabricate a substrate with matrices of holes patterned so that the flakes can be suspended and strained with the CAFM tip. We use phosphorous-doped n-type silicon wafers (n^{++}-Si) with a resistivity of (0.05-0.1 Ω·cm) from Suzhou Research Semiconductor Co. Ltd. Matrices of holes with different diameters ranging between 2 and 6 μm are patterned by Inductive Coupled Plasma Reactive Ion Etching (ICP-RIE). The depth of the holes is 2.2 μm, and each matrix is numbered so that different experiments could be conducted on the same site.

The presence of MoS_2 across the holes is verified with a Zeiss SUPRA55 Scanning Electron Microscope (SEM). The morphology is analyzed with a Veeco Multimode V AFM working in tapping mode and using silicon tips from NanoWorld (model NCH, item no. 78131F6L965). The piezoelectric effect is characterized by current maps obtained in contact mode with the conductive module of the same AFM. Additional electrical information is recorded using the Peak Force TUNA mode of a Multimode VIII AFM. For the electrical measurements we use metal-varnished silicon tips from Bruker (model SCM-PIC item no. A009/07-07/14, and SNL-10 item no. A044/09-04/13). The metallic varnish of the SCM-PIC and SNL-10 tips is Pt-Ir and Ti-Au, respectively. The nominal spring constant and resonant frequency of SCM-PIC tips are 0.2 N/m and 13 kHz, respectively. Similarly, for the SNL-10

tips the values of these two parameters are 0.12 N/m and 23 kHz. The parameters used for collecting the current maps are as follow: DC Sample bias = 0 V; Preamplifier gain = 10^9; Sensitivity = 1 nA/V. The data collected was current (amperes unit). A preamplifier with a gain 10^9 implies a load resistance is 1 GΩ, which is which is of the same order of magnitude than that used in other works.[10] The AFM images are processed with two different AFM softwares: Nanoscope Analysis 1.40 from Bruker and WSxM (version 5.0 develop 7.0) from Nanotech.

Density functional theory calculations

The above DFT calculations were conducted with the Quantum ESPRESSO code[53]. Calculations were performed using Projector Augmented Wave (PAW) atomic data sets[54-55], the Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE/GGA) exchange correlation functional.[56] A 30 Ry cut-off energy for the wave functions and a 240 Ry kinetic energy cut-off for the charge density, and an energy convergence threshold of 10^{-8} Ry. Calculations for structure (*1*) used Γ-point sampling of reciprocal space while the calculations for structure (*2*) sampled 5 points in the direction parallel to the step edges (5×1×1 *k*-point sampling). Both structures employed periodic boundary conditions as noted above.

Acknowledgments

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References

1. H. Fu, R. E. Cohen , *Nature*, 2000, **403**, 281.
2. T. Wu, H. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 4432.
3. J.J. Qi, Y.W. Lan, A. Z. Stieg, J.H. Chen, Y.L. Zhong, L.J. Li, C.D. Chen, Y. Zhang, K. L. Wang, *Nat. Commun.*, 2015, **6**, 7430.
4. X.D. Wang, J. Zhou, J. Song, J. Liu, N.S. Xu, Z. L. Wang, *Nano Lett.*, 2006, **6**, 2768.
5. O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, *Nat. Nanotechnol.*, 2013, **8**, 497.
6. N. Elvin, A. Elvin, D. H. Choi, *J. Strain Anal. Eng. Des.*, 2003, **38**, 115.
7. H. A. Sodano, *J. Intell. Mater. Syst. Struct.*, 2005, **16**, 799.
8. H. J.Xiang, J.L. Yang, J. G. Hou, Q.S. Zhu, *Appl. Phys. Lett.*, 2006, **89**, 223111.
9. B. Xiang, P.G. Wang, X.Z. Zhang, S. A. Dayeh, D. P. Aplin, C. Soci, D. Yu, D. Wang, *Nano Lett.*, 2007, **7**, 323.
10. Z. L. Wang, J.H. Song, *Science*, 2006, **312**, 242.
11. S. Xu, Y. Qin, C. Xu, Y.G. Wei, R.S. Yang, Z. L. Wang, *Nat. Nanotechnol.*, 2010, **5**, 366.
12. M. Lanza, M. Reguant, G. J. Zou, P. Y. Lv, H. Li, R. Chin, H.Y. Liang, D.P. Yu, H.L. Duan, *Adv. Mater. Interfaces*, 2014, **1**, 1300101.
13. S. Hu, C.Y. Chi, K. T. Fountaine, M. Yao, H. A. Atwater, P. D. Dapkus, N. S. Lewis, C. Zhou, *Energy Environ. Sci.*, 2013, **6**, 1879.
14. K. H.Michel, B. Verberck, *Phys. Rev. B*, 2011, **83**, 115328.
15. M. T. Ong, E. J. Reed, *ACS Nano*, 2012, **6**, 1387.
16. K. E. El-Kelany, P. Carbonnière, A. Erba, M. Rérat, *J. Phys. Chem. C*, 2015, **119**, 8966.

17. K.-A. N. Duerloo, M. T. Ong, E. J. Reed, *J. Phys. Chem. Lett.*, 2012, **3**, 2871.
18. H.Y. Zhu, Y. Wang, J. Xiao, M. Liu, S.M. Xiong, Z. J. Wong, Z.L. Ye, Y. Ye, X.B. Yin, X. Zhang, *Nat. Nanotechnol.*, 2015, **10**, 151.
19. W. Wu, L. Wang, Y.L. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T. F. Heinz, J. Hone, Z. L. Wang, *Nature*, 2014**, 514**, 470.
20. S. Manzeli, A. Allain, A. Ghadimi, A. Kis, *Nano Lett.*, 2015, **15**, 5330.
21. H. Wang, H.B. Feng, J.H. Li, *Small*, 2014, **10**, 2165.
22. A.C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, P. Bøggild, S. Borini, F.H. Koppens, V. Palermo, N. Pugno, J.A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhänen, A. Morpurgo, J. N. Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G. F. Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A. N. Grigorenko, G. Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D. Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G.M. Williams, B.H. Hong, J. H. Ahn, J. M. Kim, H. Zirath, B. J. van Wees, H. van der Zant, L. Occhipinti, A. Di Matteo, I. A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupesinghe, P. Hakonen, S. R. Neil, Q. Tannock, T. Löfwander, J. Kinaret, *Nanoscale* 2015, **7**, 4598.
23. S. Chandratre, P. Sharma, *Appl. Phys. Lett.* 2012, **100**, 023114.
24. M. Yi, Z.G. Shen, *J. Mater. Chem. A*, 2015, **15**, 5330.
25. J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. M., A. S., R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, V. Nicolosi, *Science*, 2011, **311**, 568.
26. A. O'Neill, U. Khan, J. N. Coleman, *Chem. Mater.*, 2012, **24**, 2414.
27. F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, A. C. Ferrari, *Mater. Today*, 2012 **15**, 564.
28. F. Torrisi, T. Hasan, W. Wu, Z. Sun, A. Lombardo, T. S. Kulmala, G.-W. Hsieh, S. Jung,

F. Bonaccorso, P. J. Paul, *Acs Nano*, 2012, **6**, 2992.

29. S. Agarwal, E. Yablonovitch, *Nano Lett.*, 2014, **14**, 6263.
30. D. Sinha, G. A.J. Amaratunga, *Phys. Rev. Lett.*, 2015, **114**, 147701.
31. Website of Graphene Supermarket (MoS_2 Solution) https://graphene-supermarket.com/MoS2-Pristine-Flakes-in-Solution.html
32. U. Khan, A. O'Neill, M. Lotya, S. De, J. N. Coleman, *Small*, 2010, **6**, 864-871.
33. C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, S. Ryu, *ACS nano*, 2010, **4**, 2695.
34. N. Wakabayashi, H.G. Smith, R. M. Nicklow, *Phys. Rev. B*, 1975, 12, 659.
35. P. Nemes-Incze, Z. Osvath, K. Kamaras, L.P. Biro, Carbon, 2008, 46, 1435.
36. S. Z. Butler, S. M. Hollen， L. Y. Cao, Y. Cui, J. A. Gupta, H. R. Gutie´rrez, T. F. Heinz, S. S. Hong, J. X. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, J. E. Goldberger, *ACS Nano*, 2013, **7**, 2898.
37. Y.Y. Shi,; Y.F. Ji, H. Sun, F. Hui, J.C. Hu, Y.X. Wu, J.L. Fang, H. Lin, J.X. Wang, H.L. Duan, M. Lanza, *Sci. Rep.*, 2015, **5**, 11232.
38. S. Bertolazzi, J. Brivio, A. Kis, *ACS Nano*, 2011, **5**, 9703.
39. C. Lee,; X.D. Wei, J. W. Kysar, J. Hone, *Science*, 2008, **321**, 385.
40. . C. G. Lee, Q. Y. Li, W. Kalb, X.Z. Liu, H. Berger, R. W. Carpick, J. Hone, *Science*, 2010, **2**, 328.
41. A. P. Nayak, S. Bhattacharyya, J. Zhu, J. Liu, X. Wu, T. Pandey, C. Jin, A. K. Singh, D. Akinwande, J. F. Lin, *Nat. Commun.*, 2014, **5**, 3731.
42. J. Zhang, C. Wang, C. Bowen, *Nanoscale*, 2014, **6** (22), 13314.
43. I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.
44. M. Lanza, M. Porti, M. Nafría, X. Aymerich, E. Whittaker, B. Hamilton, *Rev. Sci. Instrum.*, 2010, **81**, 106110.
45. Website of bruker (section Peak force tuna). https://www.bruker.com/cn/products/

surface-and-dimensional-analysis/atomic-force-microscopes/modes/modes/peakforce-modes.html.

46. J. Benson, M. Li, S.B. Wang, P. Wang, *ACS Appl. Mater. Interfaces,* 2015, **7**, 14113.
47. W.J. Zhang, C. P. Chuu, J. K. Huang, C. H. Chen, M. L. Tsai, Y. H. Chang, C. T. Liang, Y. Z. Chen, Y. L. Chueh, J. H. He, M. Y. Chou, L. J. Li, *Sci. Rep.*, 2014, **4**, 3826.
48. K. K. Ghuman, S. Yadav, C. V. Singh, *J. Phys. Chem. C* 2015, **119**, 6518.
49. E.L. Rosen, K. Gilmore, A. M. Sawvel, A. T. Hammack, S. E. Doris, S. Aloni, V. Altoe, D. Nordlund, T.-C. Weng, D. Sokaras, B. E. Cohen, J. J. Urban, D. F. Ogletree, D. J. Milliron, D. Prendergasta, B. A. Helms, *Chem. Sci.* 2015,**6**, 6295.
50. P.-O. Löwdin, *J. Chem. Phys.*, 1950, **18**, 365.
51. P.-O. Löwdin, *Adv. Quantum Chem.*, 1970, **5**, 185.
52. S. Helveg, J.V. Lauritsen, E. Lægsgaard, I. Stensgaard, J. K. Nørskov, B. S. Clausen, H. Topsøe, and F. Besenbacher, *Phys. Rev. Lett*. 2000, **84**, 5, 951.
53. G. Paolo, B. Stefano, B. Nicola, C. Matteo, C. Roberto, C. Carlo, C. Davide, L.C. Guido, C. Matteo, D. Ismaila, C. Andrea Dal, G. Stefano de, F. Stefano, F. Guido, G. Ralph, G. Uwe, G. Christos, K. Anton, L. Michele, M.-S. Layla, M. Nicola, M. Francesco, M. Riccardo, P. Stefano, P. Alfredo, P. Lorenzo, S. Carlo, S. Sandro, S. Gabriele, P.S. Ari, S. Alexander, U. Paolo, M.W. Renata, *J. Phys.: Condens. Matter*, 2009, **21**, 395502.
54. Wake Forest University website, AOMPAW database (online available on September 15th of 2015), http://users.wfu.edu/natalie/papers/pwpaw/man.html
55. Quantum EXPRESSO project website, simulation database, online available on September 15th of 2015, http://www.quantum-espresso.org/
56. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

Figure 1. (a) Piezoelectric ink made from liquid-phase exfoliated MoS_2. **(b)** and **(c)** SEM images of stepped multilayer MoS_2 flakes. **(d)** Topographic AFM image of a multilayer stepped MoS_2 flake. **(e)** Topographic cross section highlighted in **(d)** with a dashed line.

Figure 2. SEM images of **(a)** an uncovered hole and **(b)** two holes partially and fully covered by MoS_2. **(c)** Force distance (F-d) curve collected on the MoS_2-covered hole and on Si (inset). The points where the F-d curves are collected are highlighted in **(b)** with red/blue dots. On Si (blue dot) the F-d curve follows the typical shape on rigid substrates, but on the MoS_2-covered hole (red dot) the shape is not straight, indicating that the MoS_2 membrane is suspended. **(d)** and **(e)** AFM maps of an uncovered and fully covered hole (respectively). **(f)** Cross sections of **(d)** and **(e)** at the dashed lines.

Figure 3. Cross sections in AFM topographic maps of suspended MoS_2 using different forces. The graph shows the progressive increase of depth with the contact force. The asymmetric shape at low contact forces is related to the direction of the scan (see also Figure S4 in the Supporting Information).

Figure 4. (a) Current AFM maps measured for different contact forces, showing an increase of current. The dashed circle indicates the location of the hole. **(b)** Derivate of the topographic map collected simultaneously to panel **(a)**. The image shows multiple steps. **(c)** Cross section of a topographic map collected on the hole. The image clearly displays the multilayer nature of the suspended MoS_2 flake.

Figure 5. Calculation of the total area and volume of the current spots for the maps collected using forces of 22 nN, 112 nN, 202 nN and 247 nN (displayed in Figure 4a). Both magnitudes increase with the contact force.

Figure 6. (a) Deflection error map collected in a random location of suspended MoS_2 (inside the hole) without bias. This image displays the features of the topography, and the flake edges. **(b)** Current map collected simultaneously to (a), and therefore with zero bias, showing that the current is mainly concentrated at the flake edges. The vertical scale of **(a)** is in arbitrary

units, and the one of **(b)** is: blue 0 pA and yellow 10 pA. As the tip/sample contact area in CAFM experiments is typically ~100 nm^2, the current densities measured in **(b)** exceed 10 A/cm^2. **(c)** Overlapped cross section of a topographic and a current map collected simultaneously on suspended MoS_2, showing the correlation between steps and current peaks.

Figure 7. (a) Atomic structure of a monolayer of MoS_2 deformed to represent the experiments: yellow spheres S, pink spheres Mo. The strain-induced charge separation is shown in **(b)**. The different colours indicate the amount of excess or missing charge on each atomic site in units of the electron charge. Red colour corresponds to a negative charge accumulation of 0.015, grey is zero and blue indicates a positive charge accumulation of 0.015. The colour map is projected onto the X-Y plane for additional perspective. **(c)** Illustration of a multilayer MoS_2 sheet with stepped structure, in which both the hexagonal lattice of the MoS_2 sheet and the edges can be distinguished. For clarity, even and odd layers have been coloured with different tonalities. **(d)** DFT simulation of a tri-layer MoS_2 edge showing an accumulation of excess electron charge density at the edges (silver lobes) upon stretching along the step direction.